First-Principles Studies of Electronic Oxides

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Ceramic compounds with exploitable ferroelectric, dielectric, or magnetic properties are widely used in technical applications such as actuators, transducers, and dielectric resonators. We are using first-principles (FP) calculations to elucidate the roles of cation order-disorder and ferroelastic phenomena in dictating the phase relations and physical properties of these technologically important materials.

Ferroelectric, dielectric, magnetic, and transport properties of ceramics are typically sensitive functions of the state of cation order. Therefore, First-Principles Phase Diagram (FPPD) calculations are used to predict cation ordering phenomena and physical properties, and how they vary with chemical composition. Critical experiments are performed to test the predictions. An additional technical objective is to benchmark various FP techniques that are used for calculating physical properties (e.g. dielectric constant), and the formation energies on which FPPD calculations are based.

The intended outcome is to predict ordering behavior in complex technologically important oxide systems, with the objectives of: (1) minimizing the experimental work necessary to elucidate phase relations; (2) optimizing theoretical techniques; (3) optimizing processing strategies; (4) predicting the existence of new, technologically relevant ordered phases; (5) predicting how physical properties vary as functions of composition, temperature, and heat treatment.

The inclusion of degrees of freedom, derived from ionic motion, in the first-principles models will facilitate simulation and physical understanding of important properties. For example, the ferroelastic transitions in PZT, experimentally associated with large piezoelectricity, can be simulated as a function of temperature, composition and stress. Molecular dynamics methods, with time-varying external fields, can be used to model the dielectric properties as a function of frequency in systems of interest for microwave applications, such as $CaTiO_3$-$CaAl_{1/2}Nb_{1/2}O_3$. We have addressed several issues important to the processing and applications of electronic ceramics and accomplished several advances in the modeling of these materials.

A first-principles-based model of cation ordering in $[Na_{1/2}Bi_{1/2}]TiO_3$ has been formulated, and the ground-state ordered structure predicted. As observed experimentally, the predicted pseudocubic structure has a primitive cell with doubled cell constants in all three (x, y and z) Cartesian directions, but it has a different cation ordering configuration than the expected NaCl-related type. This is a particularly interesting result because much of the literature on $[Na_{1/2}Bi_{1/2}]TiO_3$ reports (erroneously) that NaCl-type ordering was observed. Our first-principles calculations, however, indicate that many other cation ordering configurations have lower energy than the NaCl-type.

We developed an effective Hamiltonian for the relaxor ferroelectric $PbSc_{1/2}Nb_{1/2}O_3$ (PSN), based on first-principles calculations. The model allows one to simulate the structure and dielectric properties of of PSN as a function of cation ordering, temperature, applied fields, etc. We compared the temperature dependent properties of PSN in an ordered NaCl-type Sc/Nb cation configuration with those of PSN in a random configuration, and found a significantly (35 %) lower ferroelectric transition temperature in the random state.

A working group has been formed to develop a Unified Effective Hamiltonian theory for modeling systems that exhibit both cation order-disorder and ferroelastic transitions. The first workshop was held June 2000 at NIST. The second, co-organized by B.P. Burton, will be combined with an alloy theory workshop on "Thermodynamic and Structural Properties Of Materials," and will be held in Avignon, France September 9-14, 2001. This important workshop will bring together scientists working on first-principles calculations for alloys with those carrying out analogous research on ferroelectrics and minerals.

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